

ATOM TRANSFER RADICAL POLYMERIZATION OF  
HYDROPHILIC MONOMERS IN AQUEOUS MEDIA AT  
AMBIENT TEMPERATURE

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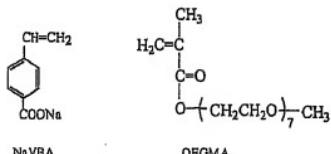
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**Introduction**

Transition metal-catalyzed living free-radical polymerization was developed independently by Matyjaszewski<sup>1</sup> and Sawamoto,<sup>2</sup> respectively. It was named Atom Transfer Radical Polymerization (ATRP) by Matyjaszewski.<sup>1</sup> In ATRP, classical combination and disproportionation are suppressed relative to propagation due to the relatively low polymer radical concentration, which is controlled by the rapid reversible equilibrium between the higher and lower oxidation states of the transition metal.<sup>3</sup> Since its discovery, ATRP has been successfully applied for the synthesis of a wide range of polymers with well-controlled structures.<sup>4</sup>

Since it proceeds by a radical mechanism, ATRP is tolerant of protic species. Thus, Matyjaszewski<sup>1</sup> and Sawamoto<sup>2</sup> have both shown that the addition of water does not impede ATRP in non-aqueous media. Moreover, Matyjaszewski reported that hydroxethyl acrylate (HEA) could be homopolymerized in aqueous solution at 90°C.<sup>5</sup> Recently, our group has successfully carried out aqueous ATRP of sodium methacrylate with reasonable control over molecular weight and molecular weight distribution.<sup>6</sup> The success of aqueous ATRP promises new routes to the synthesis of water-soluble polymers with well-defined architectures.

We report herein the successful ATRP of two more hydrophilic monomers, NaVBA and OEGMA, in aqueous media at ambient temperature.



**Experimental**

**Synthesis of the Initiators**

Initiator (1) in Scheme 1 was synthesized by reacting a near-monodisperse, monomethoxy-capped oligo(ethylene oxide) ( $M_w^{\text{P}} \approx 7$ ) by <sup>1</sup>H NMR spectroscopy and  $M_w/M_n \approx 1.10$  by GPC with 2-bromoisoobutyryl bromide at 0°C in the presence of triethylamine according to a literature procedure.<sup>7</sup> Initiator (2) was converted from α-bromo-*p*-toluic acid by adjusting solution pH to 11. Initiator (3) was synthesized by reacting vinyl bromoacetate with 2-(dimethylamino)ethyl 2-bromoacrylate. The latter had been synthesized by reacting a dimethyl hydroxethyl amine with bromoisobutyryl bromide.

**Polymerization**

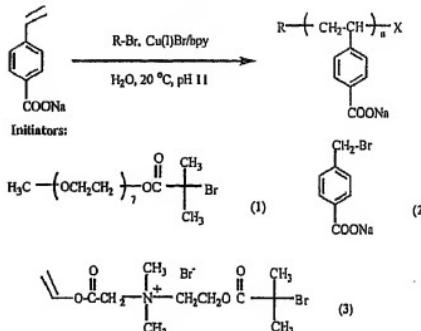
A typical polymerization was carried out as follows: Initiator (2) (0.34 mmol, 1 equiv.) was dissolved in 5 mL doubly distilled water with the addition of NaOH. To this degassed solution was added the 2, 2'-bipyridine (Bpy) ligand (0.68 nmol, 2 equiv.), followed by Cu(I)Br (0.34 mmol, 1 equiv.). An aqueous degassed solution (20 mL) containing NaVBA (5.0 g; 34 mmol; 100 equiv.) at pH 11 was added to this stirred reaction solution at 20 °C using a double-tipped needle. The reaction solution rapidly became dark brown and much more viscous, indicating the onset of polymerization; exotherms of 5–10 °C were typically observed. In order to terminate the polymerization, the reaction solution was first diluted with water (10 mL) and then added to 3 M HCl (300 mL). The resulting white precipitate was isolated by filtration and dried in a vacuum oven at 20 °C for 16 h.

**Polymer characterization**

Monomer conversion was measured using <sup>1</sup>H NMR. Molecular weight distributions were assessed using gel permeation chromatography (either 1.0 M NaCl eluent containing 50 mM Tris buffer at pH 9; PEO standards; RI detector or THF eluent, PMMA standards, RI detector). In the later case, the NaVBA homopolymer was first converted into its methyl ester using excess methyl iodide in THF at 20°C in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU);<sup>8</sup> the degree of esterification was at least 98% as judged by <sup>1</sup>H NMR spectroscopy. Intensity-average micelle diameters were measured using PCS.

**Results and Discussion**

The polymerization of NaVBA were carried out using various initiators, see Scheme 1. Reaction yields, polymer molecular weights and polydispersities are summarized in Table 1.



Scheme 1

Table 1 Summary of results for the homo polymerization of NaVBA using ATRP in aqueous media at 20°C

Initiator	Time/h	Yield %	$M_{\text{w}}$	$M_{\text{z}}$	$M_w/M_z$
1	16.0	99	9600	9400	1.28
2	0.5	95	13800	13400	1.32
3	1.0	80	7000	7400*	-----

a: Calculated from <sup>1</sup>H NMR spectra

Figure 1 shows a typical conversion vs. time curve. Very high conversions of monomer to polymer were achieved with initiator (2) within short reaction times (< 0.5 h) and the polymerization followed first order kinetics at all conversions. On the other hand, curved semi-logarithmic plots were obtained for initiators (1) and (3), indicating more complex kinetics. Although high yields were eventually obtained (see Table 1), much slower polymerizations were obtained for these latter initiators compared to initiator (2). Narrow polydispersities, which are indicative of a living polymerization, were obtained for initiators (1) and (2). Finally we note that, since styrene monomers can be polymerized via ATRP selectively in the presence of vinyl acetate groups, using initiator (3) leads to the formation of novel, well-defined acidic macromonomers.

Inspection of the <sup>1</sup>H NMR spectra ( $\text{D}_2\text{O}$ ) of the purified NaVBA homopolymer prepared using initiator (1) confirmed the presence of the initiator fragment, as expected. The peak integral of the ethylene oxide protons at 3.4 ppm was compared to that due to the aromatic protons of the NaVBA residues at 6.8–6.9 ppm in order to determine the number-average degree of polymerization of the NaVBA chains by end-group analysis (such NMR calculations proved impossible for polymers prepared using initiator (2) since its aromatic protons were indistinguishable from those of the NaVBA residues). This approach yielded final  $M_{\text{z}}$  values which were in excellent agreement with those calculated from the corresponding monomer/initiator

ratios. Furthermore, the evolution of  $M_n$  with conversion was linear, as expected for a living polymerization (see Figure 2).

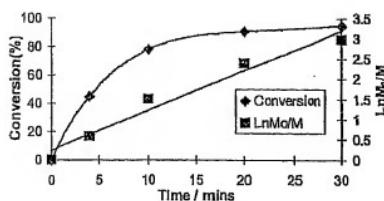


Figure 1 Kinetic data for the polymerization of NaVBA with (2)CuBr/bpy in water at 20°C.  $[\text{NaVBA}]_0=1.36\text{M}$ ;  $2[\text{Initiator}]_0=2[\text{Cu}(1)\text{Br}]_0=([\text{bpy}]_0=0.0272\text{M}$ ; pH 11

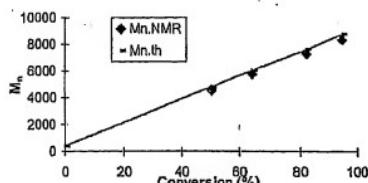


Figure 2 The evolution of molecular weight with monomer conversion during the polymerization of NaVBA with (1)CuCl/bpy in aqueous media at 20°C.  $[\text{NaVBA}]_0=1.36\text{M}$ ;  $2[\text{Initiator}]_0=2[\text{Cu}(1)\text{Br}]_0=([\text{bpy}]_0=0.04\text{M}$ ; pH 11

Using a similar protocol, the "living" polymerization of OEGMA in aqueous media at 20°C was achieved within 20' minutes.<sup>10</sup> In a control experiment, the bulk polymerization of OEGMA with (1)CuCl/bpy at 20°C will cost more than 15 hours to achieve high conversion (Figure 3) and polymerization is controllable (Figure 4). The results imply that water strongly affect the polymerization of OEGMA.

Diblock copolymers were successfully synthesized by sequential monomer addition, either with OEGMA as the first monomer or NaVBA as the first monomer, which further demonstrates the living character of aqueous ATRP. The results are summarized in Table 2. Since these are 'one-pot' syntheses, there is a tapered statistical sequence at the block junction point.

Table 2 The results of block copolymer syntheses

entry	First monomer	Target NaVBA content (mol%)	NMR NaVBA content (mol%)	$\text{M}_w/\text{M}_n$
1	NaVBA	75	70	1.28
2	OEGMA	43	45	1.30

In the case of entry 2, reversible self-assembly was observed in aqueous media on adjusting the solution pH from pH 8 to pH 3. On protonation, <sup>1</sup>H NMR studies confirm that the styrenic block becomes hydrophobic and forms the dehydrated micelle core, with the OEGMA block forming the solvated micelle corona. The intensity-average micelle diameter was approximately 20 nm, as judged by PCS. However, an NaVBA-rich diblock copolymer (see entry 1), flocculated at pH 3. This is because the OEGMA chain is too short to form stable micelle.

In conclusion, it has been shown that NaVBA and OEGMA undergo well-controlled ATRP at ambient temperature in aqueous media. Further details of this study, such as the effect of monomer and catalyst concentration on the rate of polymerization have also been investigated.

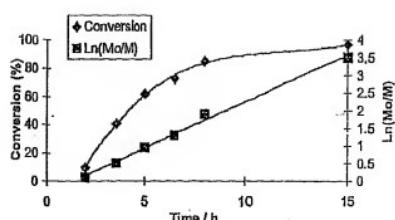


Figure 3 Kinetic data for the polymerization of OEGMA with (1)CuCl/bpy in bulk at 20°C.

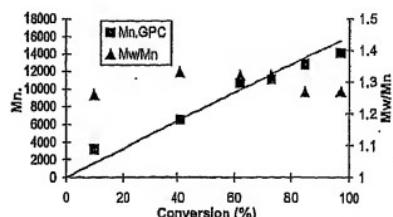


Figure 4 The evolution of molecular weight and molecular weight distribution with monomer conversion during the polymerization of OEGMA with (1)CuCl/bpy in bulk at 20°C.

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